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EFFECTS OF REDUCED FRESH WATER USAGE ON ION BUILDUP IN A TYPICAL PAPER MACHINE WATER SYSTEM

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ABSTRACT

The recently-developed equilibrium feature of MAPPS was used to determine the effects on the ionic concentrations in a typical paper machine system as a result of reducing the inflow of fresh water. The effects of reusing water internally were also determined. This report describes the effects on four typical ions, i.e. sodium, calcium, chloride, and iron in each of three types of internal fiber or water streams: dilution water, diluted stocks and broke stocks as fresh water flow is reduced by 90%. Results are shown for two limiting cases, (1) adsorption does not change within the water system and (2) equilibrium and adsorption do occur.

In the first situation, the levels of bound ions do no change and the free forms of the two ions increase significantly while the free forms of the other two ions do not increase. Ions which are introduced into the main dilution cycle (in this case sodium and sulfate) increase considerably while ions which are introduced in the broke cycle (calcium and chloride) do not. A reduction in fresh water also reduces a significant source of ions into the system.

The case where equilibrium is assumed to occur is somewhat more complex. The ions which bind more tightly to pulp fibers such as iron and calcium shift to the bound forms and leave primarily with the paper. Thus there are more routes to purge the ions from the system. As a result, only sodium increases significantly and this occurs only in the broke system. There are actual declines in the bound forms of the components as fresh water flow increases. The free forms do not change greatly in this case. The ion concentrations would have shown a much larger increase if a portion of the wash water had been recycled internally. If all the wash water were recirculated, the ion concentrations would build up until the flow out in the form of ash in the sheet balanced the flow in. This upper limit has not yet been determined. However, the concentration could readily be determined based on the dry fiber flow and the consistency at the end the wire or press section.

INTRODUCTION

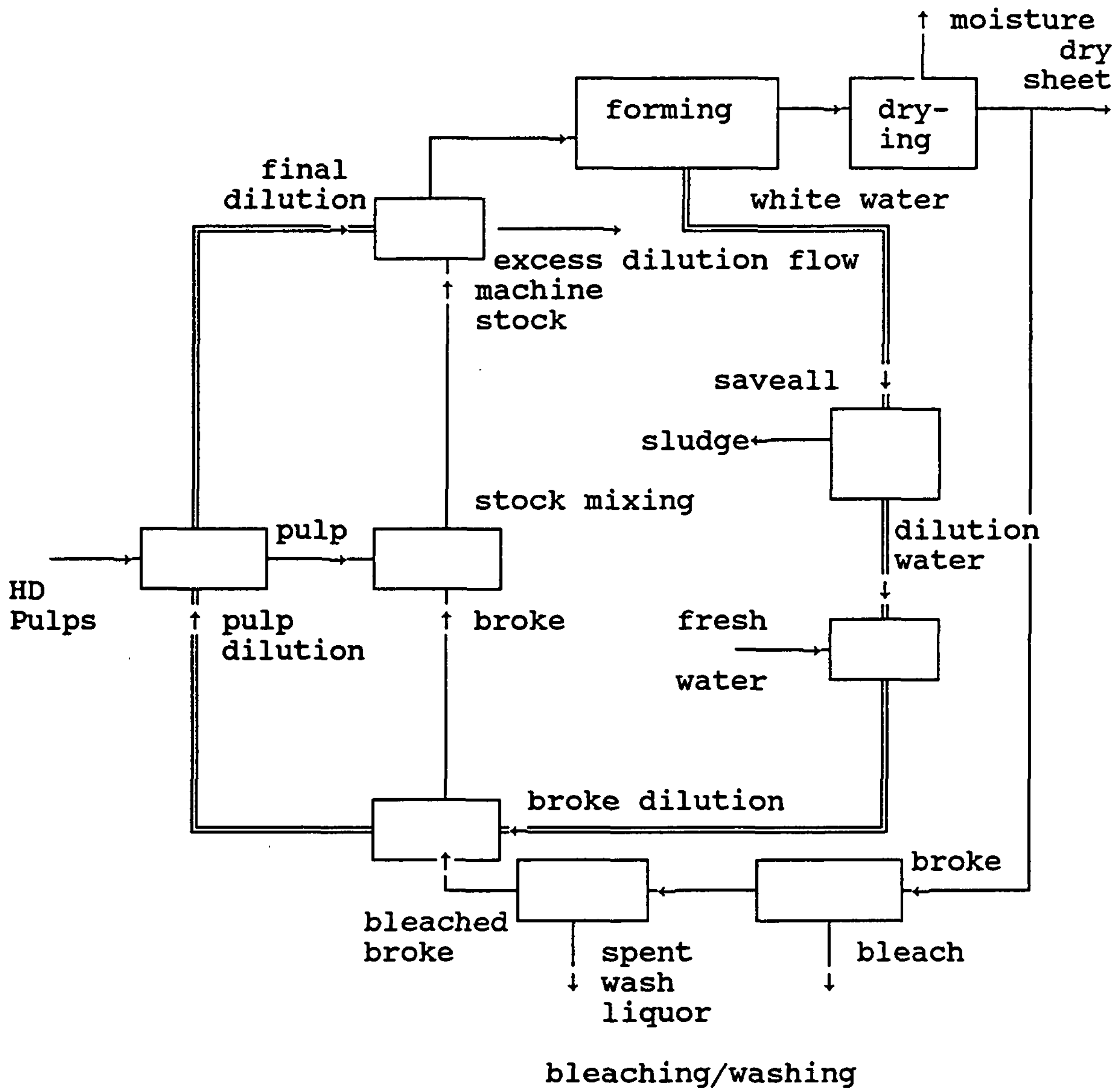
An equilibrium calculation system has been developed to quantify the effects of water reuse and water closure on the mill environment. This new system is part of the MAPPS simulation program developed by the Institute. To use the system it is only necessary to add an equilibrium block (EQUIL) to the process flowsheet at each point where equilibrium information is needed. The stream entering the EQUIL block is then broken down internally into basic components and then reconstructed into the equilibrium composition at that point. The system computes the pH, ionic strength, precipitates which may form and the sorption of ions to the pulp fibers. The effect of gas partial pressure is also taken into account although only carbon dioxide is included. The block displays and prints out the equilibrium composition, all the various species present and the distribution of the basic components among the various species.

This report illustrates some of the effects of reduced water inflow on the equilibrium buildup in the water systems of a typical paper machine. The results are based on a detailed model of the paper machine which included the stock preparation, forming, drying and white water recovery, and bleaching systems. All process input streams were taken into account including additives which may have contributed to the ions entering the system. Samples of sixteen internal water and pulp streams were analyzed for bound and soluble forms of sodium, calcium, magnesium, iron, sulfate and chloride. The concentrations of the bound and free forms were matched by adjusting the absorption constants in the model. Four different pulp sources both hardwood and softwood including broke were included.

Approximately 95% of the calcium, 99% of the magnesium, and 50 to 70% of the iron is bound to the fibers while a much smaller percentage of the monovalent cations and anions are bound. A similar trend was seen with other fiber streams throughout the water system. This behavior is consistent with observations in the literature. These three ions were more tightly bound and probably do not participate in equilibrium to the extent that the other ions do. To handle this situation, the fraction of irreversible binding was specified and these ions were not allowed to equilibrate with the pulp. This was accomplished by removing the equilibrium reactions between these ions and the pulp from the data base.

A conceptual flow diagram of a typical papermachine white water system is shown in Figure 1.

Figure 1. Typical Water and Fiber Flow Schematic in a Papermaking System



Pulps and additives including acids and bases serve as the main sources of trace metals and anions. An additional source of trace ions is through fresh water addition which contributes typical hard water components such as calcium, magnesium, sodium and chloride in proportion to the degree of hardness of the water.

Fresh water typically enters into the saveall system or as showers around the paper machine. In both cases this fresh water also ends up in the saveall system. Metals leave the system in a variety of ways. Bound forms leave primarily with the sheet or with the sludge from the save all. Dissolved forms leave with the sheet, with the spent wash liquor or with the various overflows and sewer streams. The sludge accounts for very little of either the free or bound forms. The so-called dissolved forms become associated with the pulp in the drier as water is removed and are not volatilized.

The primary feedback loops in the process are created by use of treated water as stock dilution in the machine approach system and in the broke system. A major water loop can be defined as beginning with the various pulp dilution stages, passing to the white water down-comers and into the saveall and then into the dilution water system and back to the dilution stages. A second feedback loop is the broke which may or may not be bleached but is in any case returned to the fiber line at some point. A third potential feedback loop is the reuse of water. In the system discussed here, wash water is not reused. This provides a significant purge to the water system.

Ion buildup will depend on the relative balance between the addition and the removal of ions from the system. Fresh water can be reduced to the extent that other high quality water is available and to the extent that the process can tolerate increased ion concentration. For example, excess treated water after dilution can be diverted to the showers or to the pulp seal system to replace fresh water. Tank overflows which are sewered can also be reduced. These diversions can be used to reduce the flow of fresh water to the system. After sewers and overflows have been reduced to zero and all excess treated water is used, no further decrease in fresh water can be made without increasing the consistencies of the various dilution stages. If fresh water is not used for washing the pulp and spent wash liquor is not reused, the opportunities to substitute for fresh water become quite limited.

The fiber line is actually quite open since fiber passes more or less directly from the high density chests to the dry end of the papermachine. Feedback occurs mainly through broke recycle. Addition of calcium will tend to increase the bound forms of calcium. Washing will not remove all of the tightly bound cations such as calcium, magnesium or iron. Extractable ions such as sodium will be more easily removed. Recirculation of wash liquor will tend to concentrate certain species in the water phase. The higher water phase concentrations will also lead to increased sorption. Simply diluting the feed with spent wash liquor and then thickening will not remove bound ions very effectively since sorption levels may increase rather than decrease.

The tolerance of the process to increased ion concentration will vary considerably. Chloride ions will affect corrosion rate and will play an important role in how closed the system can become. Also tolerance to increased salts in the sheet may also limit the degree of closure. Some of these implications are shown in Table 1.

Table 1

Some Effects of Increased Water Closure	
Effect	Cause
Increased Corrosion Rates	Higher chloride levels
	Higher temperatures
Retention shifts	pH shift
Sheet properties deteriorate	Higher sheet ash
Deposits buildup	Higher salt levels

The conventional myth is that as the recycle ratio increases, the levels of ions in the process will increase. However, this may not always be the case. In the following sections, we will explore the notion of closure and try to sort out fact from fiction.

CASE STUDIES

For illustrative purposes, two limiting cases are described. In one case equilibrium is not taken into account within the water system and no interactions between liquid phase components and pulp occurs. All bound and free forms entering the system are based on the equilibrium composition on the entering pulps. Another way of stating this case is that there is no change in the degree of binding onto the pulps in the circulation system. In the second case equilibrium is assumed and the tightly bound ions are irreversibly bound while the more loosely bound ions adjust to the local conditions based on specified equilibrium constants.

There are three primary areas to consider: (1) the low consistency flows such as white water, saveall feed water and dilution water, (2) the stock streams such as the machine stocks to the paper machine, and (3) the flow into and out of the bleaching and washing area, the diluted feed, spent wash liquor and high consistency mat. The effects of reduced fresh water feed will be shown on the concentrations of key ions such as sodium, chloride as well as calcium and sulfate in each of these three areas.

In-flow of Fresh water

As mentioned earlier, fresh water in-flow can be reduced to the extent that there is excess dilution water and overflows and other discharges to the sewer can be eliminated. In the present case, the excess dilution water is significant and there are other losses to the sewer. A new steady state is reached when the water flowing in as fresh water plus the water entering with the HD stocks equals the outflows from the saveall with the sludge and in the washer system with the spent bleach liquor. In the present case this amounts to a reduction of nearly 90% in the fresh water feed.

Case 1: Equilibrium is ignored

Effect on the levels of Bound Ions

When equilibrium is not considered, the levels of bound ions in all the streams are constant as fresh water flow decreases. Ash levels increase by only 20% as the fresh water is reduced. This increase is approximately the same as the dilution effect of the fresh water on the total dilution water.

The following figures show the relative changes in ion concentrations resulting from a reduction in fresh water feed to the system. For illustration purposes, the concentrations are normalized with respect to the initial concentration of that ion in the bleached broke mat stream which generally contains the highest concentrations. Values less than 1 indicate that the concentrations are less than that of the bleached broke mat and values greater than one indicate concentrations greater than the initial bleached broke mat. Because the dilution water and diluted stock concentrations are significantly lower than those of the bleach stock, the values for these streams are multiplied by 10.

Effect on Dilution Water Quality

Figures 2 through 5 show the increase in calcium, chloride, sodium and sulfate ion concentrations in the dilution or treated water from the saveall indicated by the "x" increase from 0.55 to 1.0 for the calcium levels. The chloride levels change very little while the sodium and sulfate levels increase by 100 to 300%, respectively. It is interesting that the initial reduction in fresh water flow only leads to a relatively small increase while the large change results from the last 20% reduction. The chloride levels don't change as much as the other ions because chloride is introduced primarily in the bleach which is washed out before entering the main water loop. On the other hand, acid and base introduce sulfate and sodium ions into the main water loop which tends to stay in the loop and become more concentrated as the fresh water flow is reduced.

Except for the sulfate ions, initially the ion concentrations in the diluted stocks and dilution water are 50 to 80% of the mat concentration. However, as fresh water is reduced, the concentrations in these more dilute streams approach that in the broke mat. In the case of chloride, all the concentrations increase slightly about the same amount and there is not much effect. This is due to the effects of washing after bleaching. If chloride were bound to the pulp in the bleaching step, less chloride would be washed off and more would enter the main loop leading to a greater buildup.

Effects on the Diluted Stocks

Figures 2 through 5 show the effects of reduced fresh water on the ions in the two diluted stocks. In this case the change in ion concentrations in the diluted stocks reflected the changes in the dilution water. This is to be expected since the only way to introduce ions to the fiber stock is through dilution or the mixing of stocks such as the broke.

Effect on the Streams Leaving the Bleaching and Washing

As with the diluted stocks, the mat and other streams leaving the washing stage increase dramatically in concentration as water flow is reduced from 70 to 90%. This is mainly from the composition of the broke which is the mixture of all the stocks and thus reflects the change in the dilution water composition.

Effects on Ash Levels

Although not shown, the ash level in the dry sheet increases about 20% due to the increased ions remaining with the sheet at the dry end of the machine. If the sheet de-waters to 28% consistency and there is no pressing, then 72% of the total flow leaving the papermachine was water. As the concentration in the diluted stocks increases, this change will show up as an increase in ash level.

Case 2: Equilibrium Considered

Effect on the levels of Bound Ions

When equilibrium is taken into account, the levels of bound ions in all the streams change significantly as fresh water flow decreases. In most cases, the level of bound ions increases while in a few situations the level decreases. In contrast to the previous example, the free forms of the ions do not change significantly as the fresh water flow is decreased. For this reason, only bound forms of calcium, chloride, sodium and sulfate are shown in Figures 6 through 9.

Effect on Dilution Water Quality

As mentioned previously, the concentrations of free ions in this case do not change greatly as water flow increases. However, the sodium levels increase about 10%, while the other ions change very little. Since there is no fiber present in the dilution water, the levels of bound ions are not relevant.

Effect on Diluted Stocks

About the only major change in bound ion concentrations occurs with sodium, the broke or diluted stocks which increases by several hundred percent. In the case of sulfate ion, the concentrations actually decrease somewhat as the fresh water flow decreases. This is due to the reduction in the source of sulfate ions from the fresh water. Bound calcium increases about 20% in the broke while the changes in the diluted stocks are very slight. This is a result of the small change in the dilution water composition. For chloride, sodium and sulfate ions, the concentrations decrease very slightly due to the reduced contribution of fresh water. Calcium increases in the broke due to the contribution from bleaching chemicals.

CONCLUSIONS

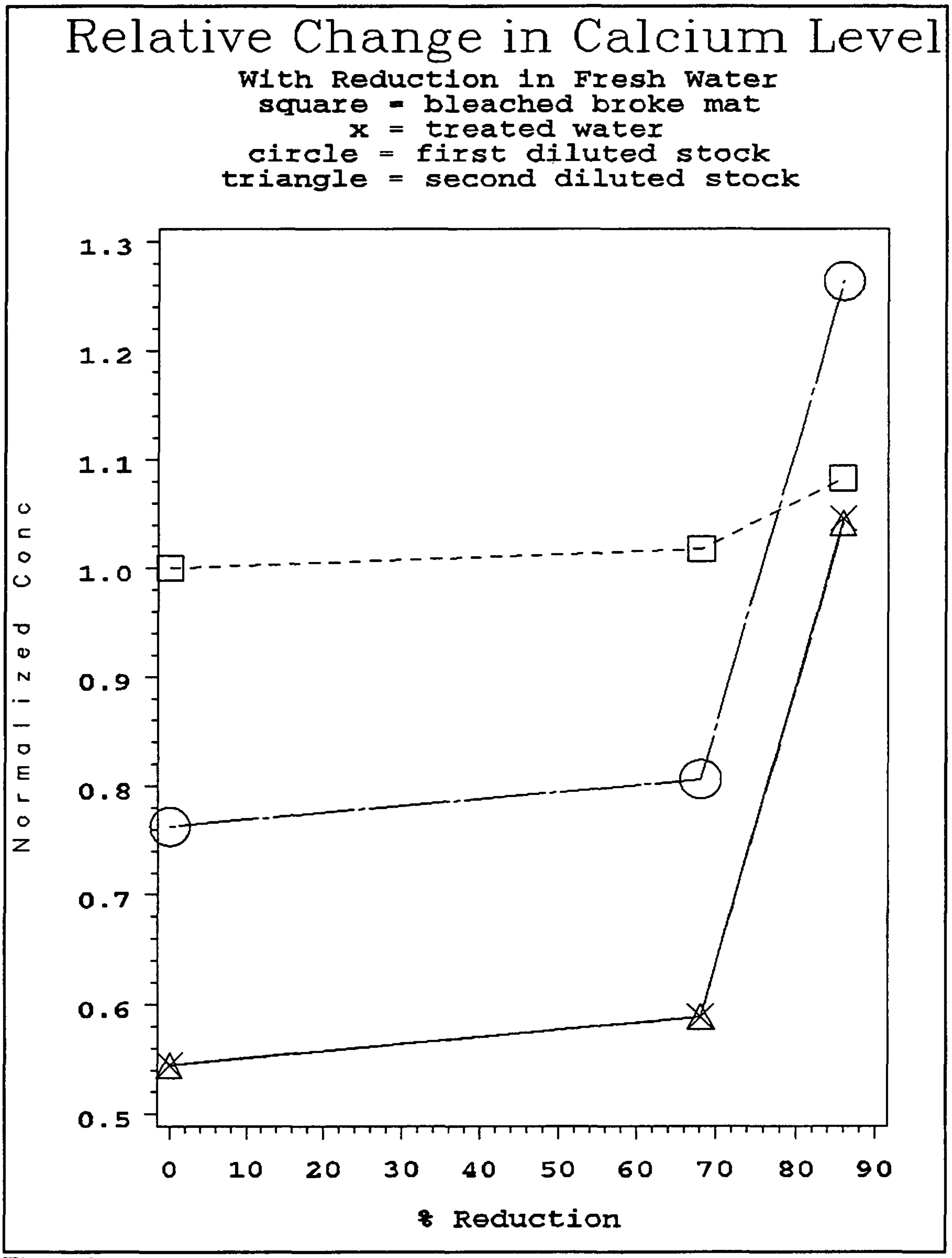
The equilibrium feature of MAPPS is a powerful tool to investigate the effects of water reuse and to determine the most effective means of reducing water usage while minimizing the impact on the mill environment. In many cases, significant opportunities may exist to reduce fresh water usage.

FUTURE WORK

Future reports will describe alternative uses for internal water and the effects on stream concentrations.

ACKNOWLEDGEMENTS

This work was made possible through funds provided by members of the Institute of Paper Science and Technology.



Relative Change in Calcium Level
With Reduction in Fresh Water
square = bleached broke mat
x = treated water
circle = first diluted stock
triangle = second diluted stock
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
Normalized Conc
0
10
20
30
40
50
60
70
80
90
% Reduction

Figure 2

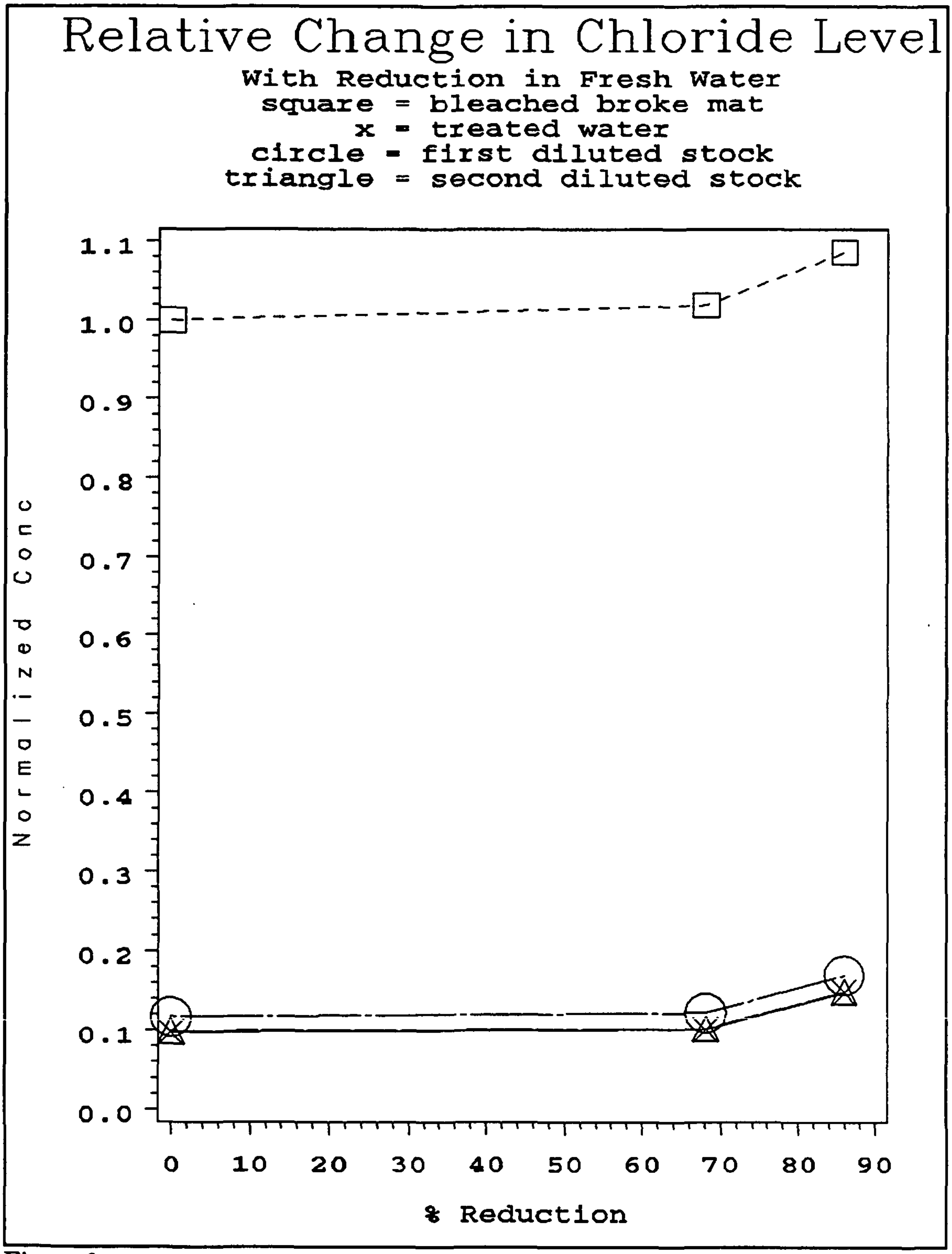

Relative Change in Chloride Level
With Reduction in Fresh Water
square = bleached broke mat
x = treated water
circle = first diluted stock
triangle = second diluted stock
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Normalized Conc
0
10
20
30
40
50
60
70
80
90
% Reduction

Figure 3

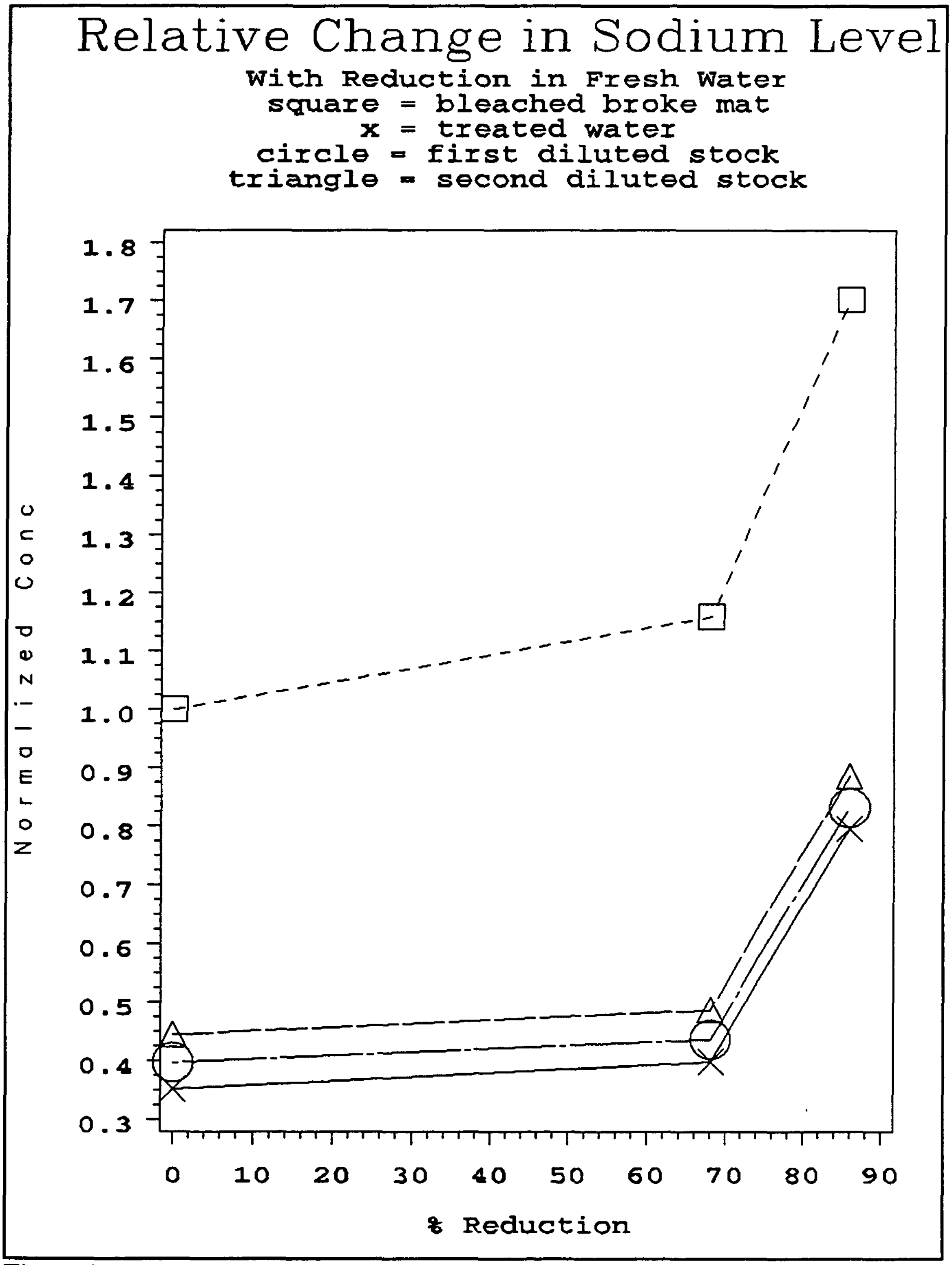

Relative Change in Sodium Level
With Reduction in Fresh Water
square = bleached broke mat
x = treated water
circle = first diluted stock
triangle = second diluted stock
Normalized Conc
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0 10 20 30 40 50 60 70 80 90
% Reduction

Figure 4

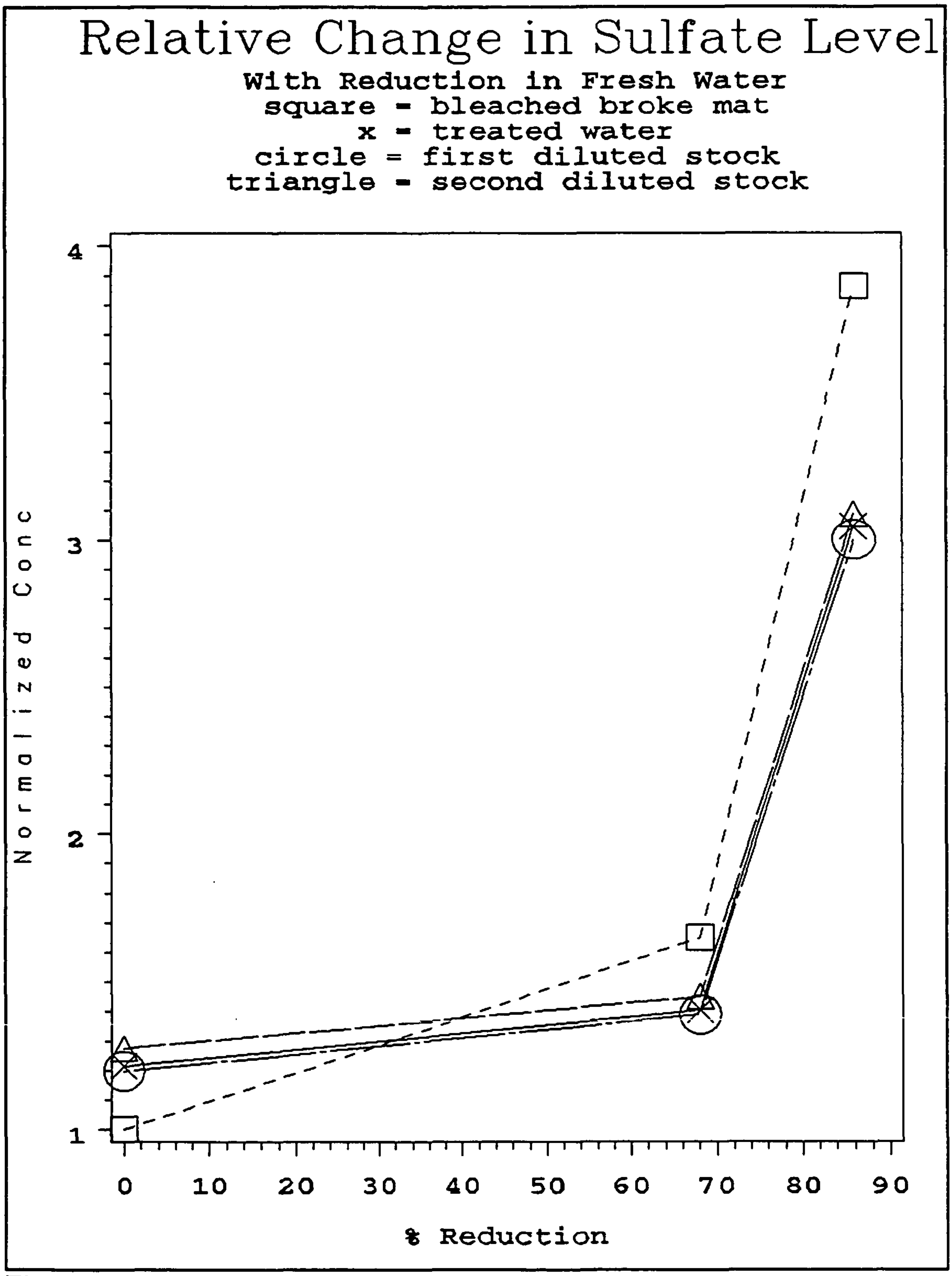

Relative Change in Sulfate Level
With Reduction in Fresh Water
square = bleached broke mat
x = treated water
circle = first diluted stock
triangle = second diluted stock
Normalized Conc
1
2
3
4
0
10
20
30
40
50
60
70
80
90
% Reduction

Figure 5

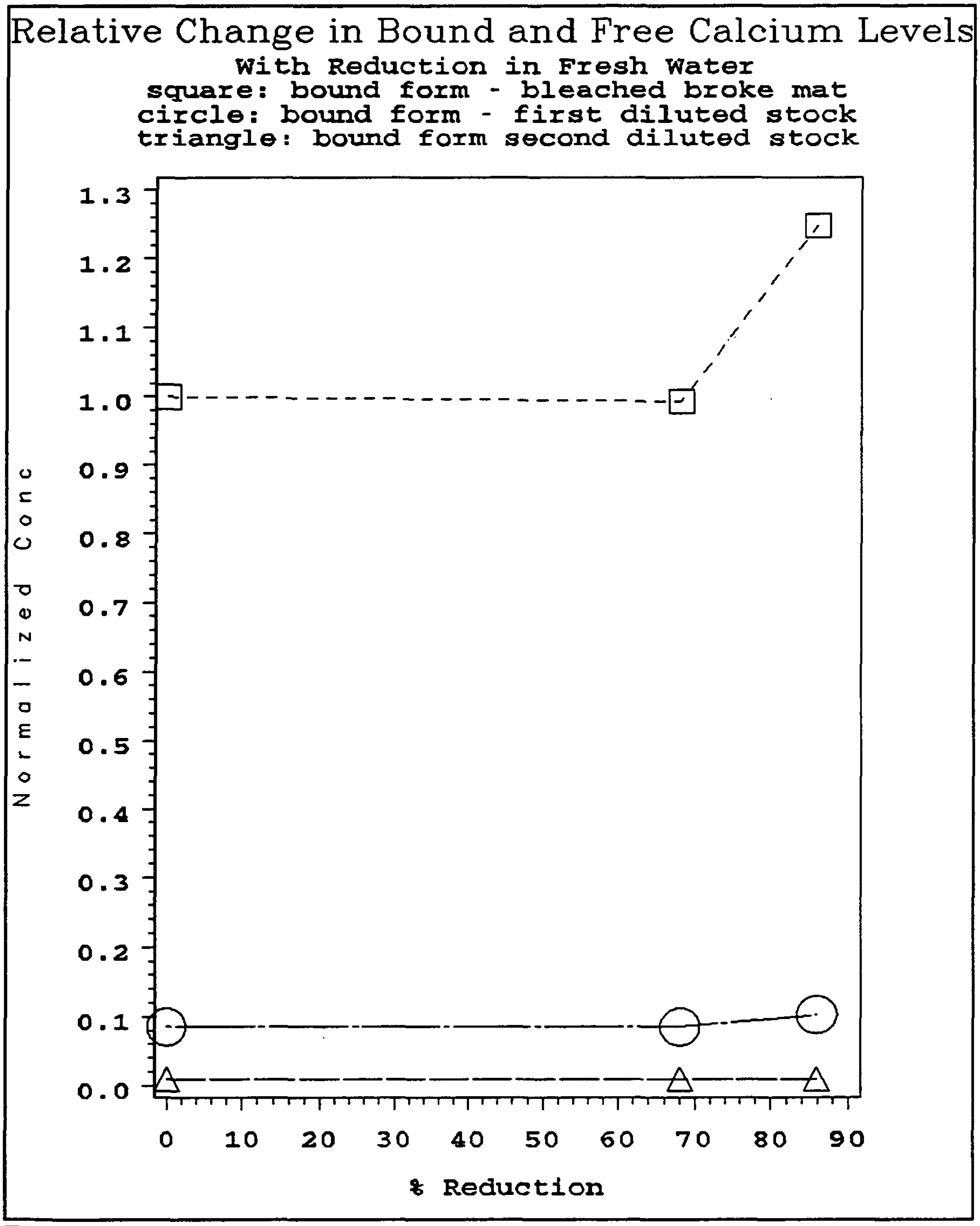

Relative Change in Bound and Free Calcium Levels
With Reduction in Fresh Water
square: bound form - bleached broke mat
circle: bound form - first diluted stock
triangle: bound form second diluted stock
Normalized Conc
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
10
20
30
40
50
60
70
80
90
% Reduction

Figure 6

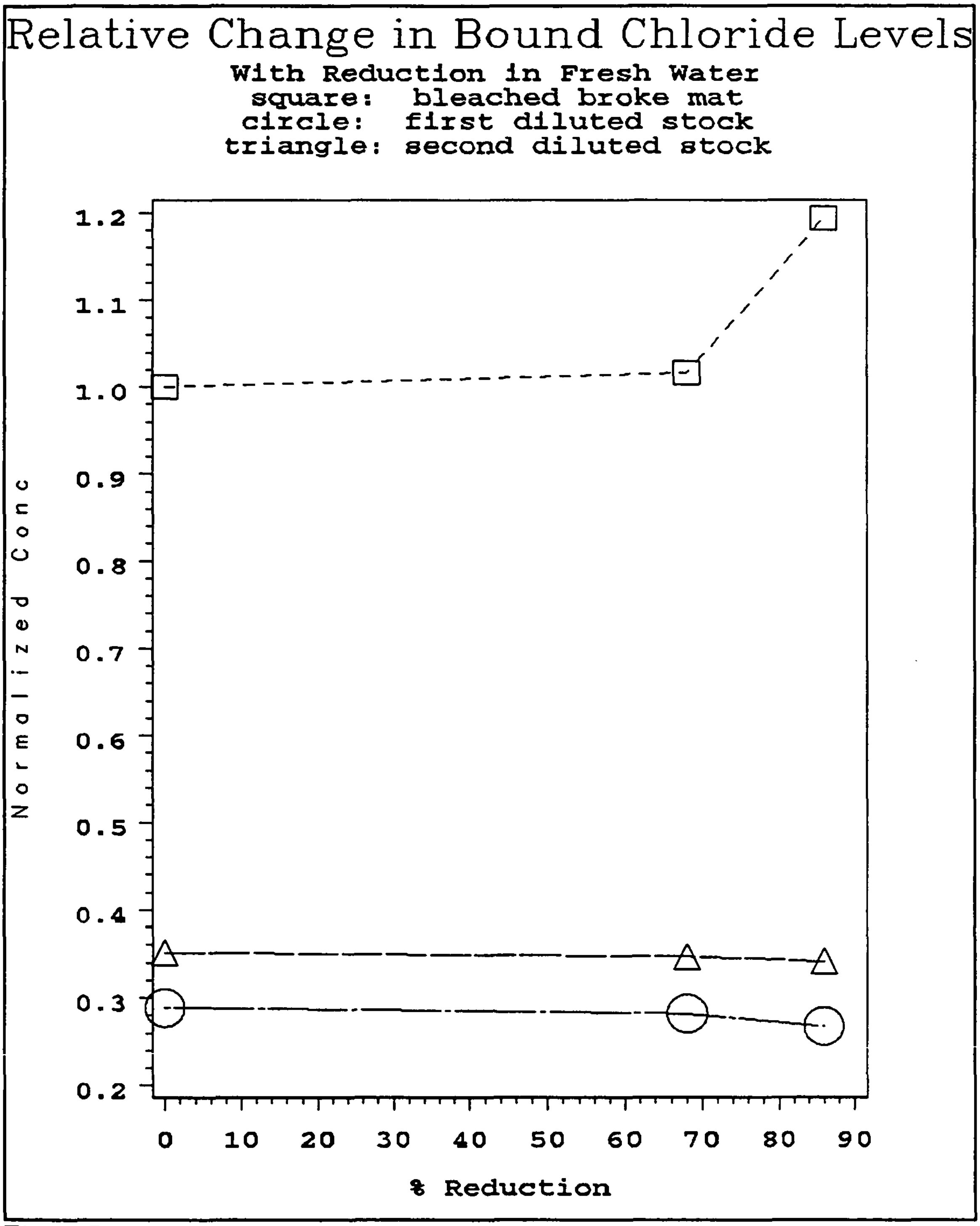
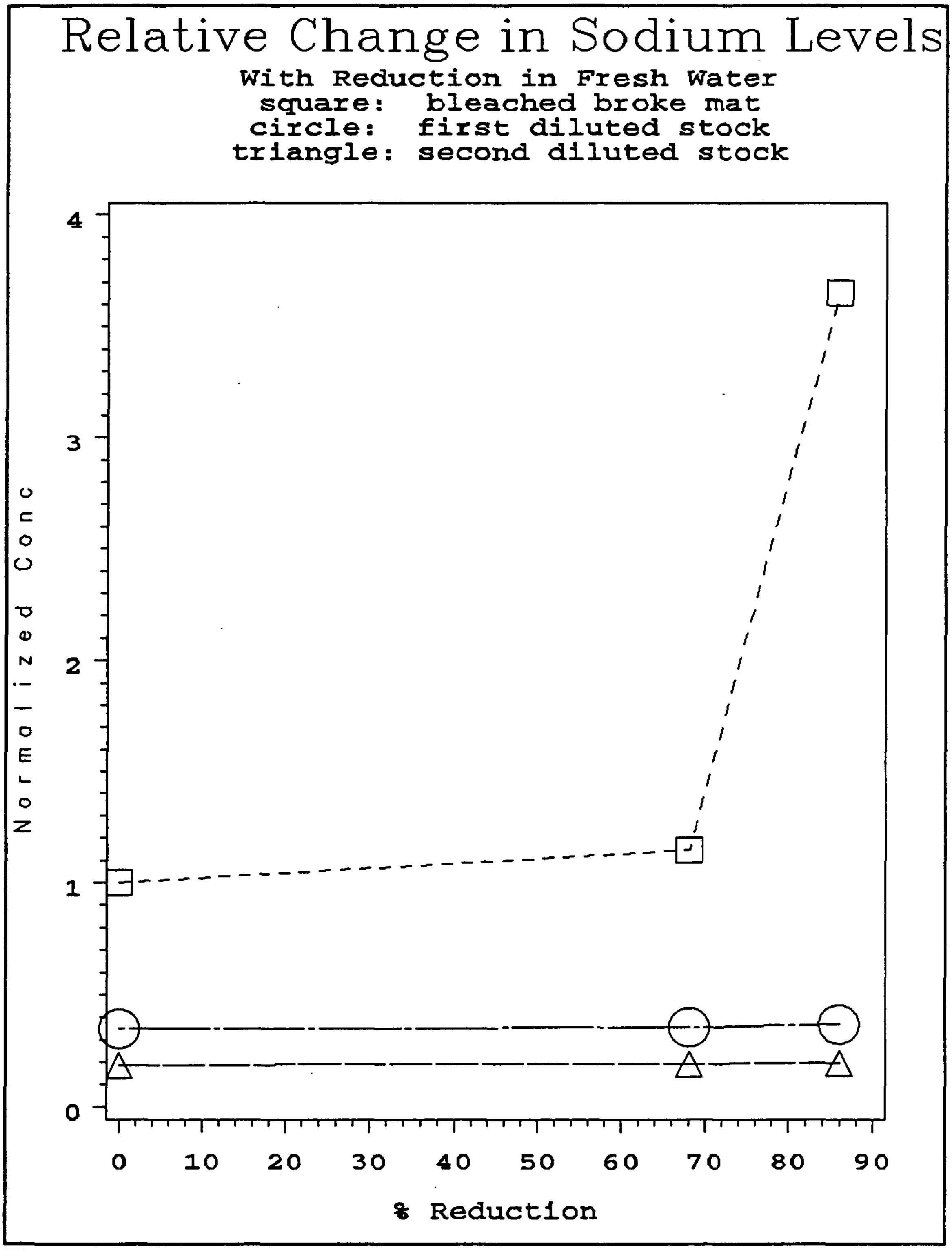
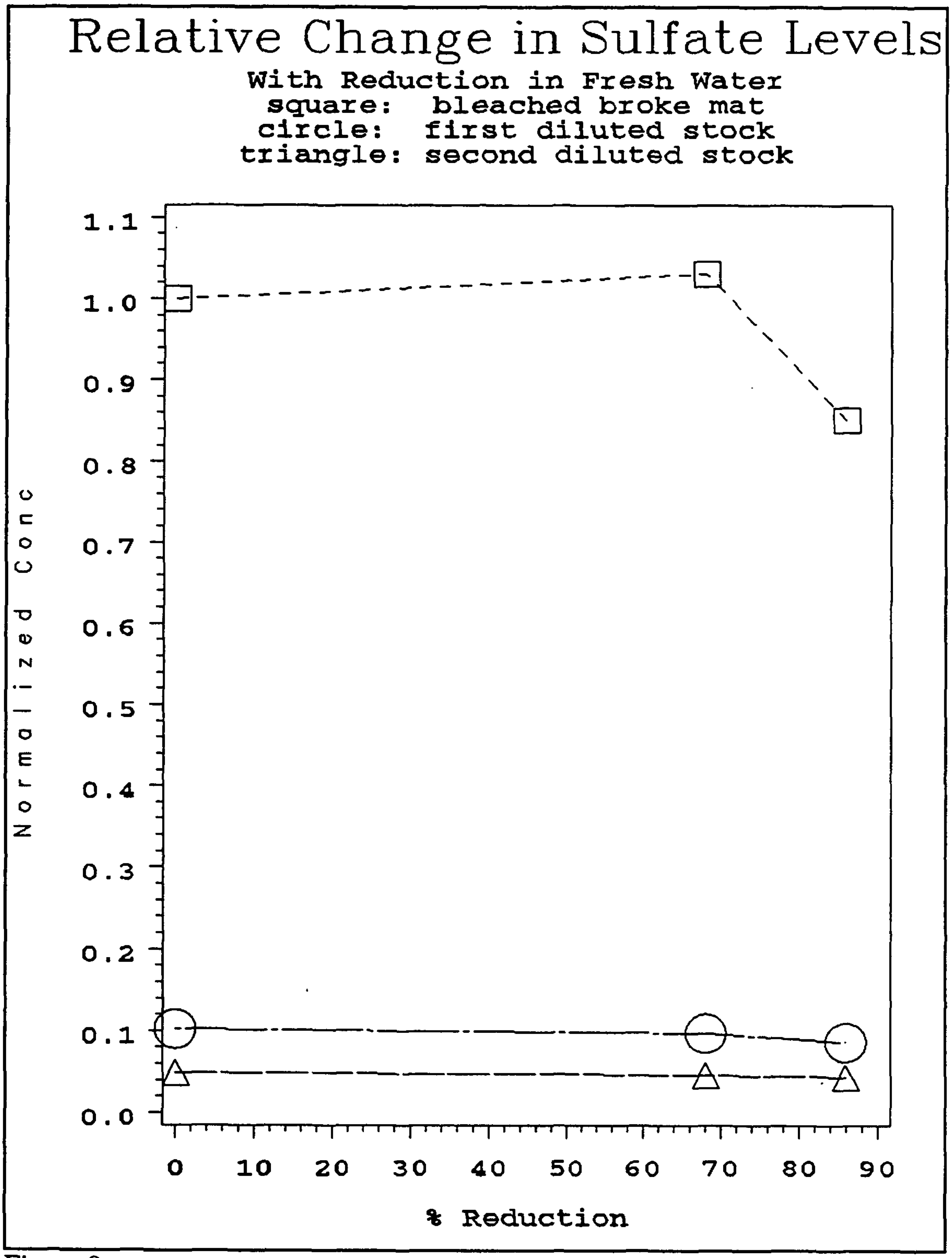

Relative Change in Bound Chloride Levels
With Reduction in Fresh Water
square: bleached broke mat
circle: first diluted stock
triangle: second diluted stock
Normalized Conc
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0
10
20
30
40
50
60
70
80
90
% Reduction

Figure 7



Relative Change in Sodium Levels
With Reduction in Fresh Water
square: bleached broke mat
circle: first diluted stock
triangle: second diluted stock
Normalized Conc
0
1
2
3
4
0 10 20 30 40 50 60 70 80 90
% Reduction

Figure 8



Relative Change in Sulfate Levels
With Reduction in Fresh Water
square: bleached broke mat
circle: first diluted stock
triangle: second diluted stock
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Normalized Conc
0
10
20
30
40
50
60
70
80
90
% Reduction

Figure 9